# THE REMOVAL OF CHROMIUM FROM SYNTHETIC TANNERY WASTEWATER USING ACTIVATED CARBON

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# THE REMOVAL OF CHROMIUM FROM SYNTHETIC TANNERY WASTEWATER USING ACTIVATED CARBON DEVELOPED FROM PARTHENIUM STEM


**BY**

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**JANUARY 2019**

# Declaration

I hereby declare that this thesis entitled **"Removal of Chromium from synthetic tannery wastewater using activated carbon developed from parthenium stem"** was composed by myself, with the guidance of my advisor, that the work contained herein is my own except where explicitly stated otherwise in the text, and that this work has not been submitted, in whole or in part, for any other degree or professional qualification.

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# Certificate

This is to certify that the thesis prepared by **Mr. Dinaol Bedada Dibaba** entitled **"Removal of Chromium from synthetic tannery wastewater using activated carbon developed from parthenium stem"** and submitted in fulfillment of the requirements for the Degree of Master of Science complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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# Abstract

*Wastewater released in to environment from industrial sector without proper treatment cause impacts on environment and humans. One of the industry sectors that can produce a large quantity of wastewater is leather tanning industry. The wastewater from this industry has heavy metals and must be treated before released to the environment. Chromium is one of the popular chemical widely used in leather tanning industry. So, the wastewater from this industry has high amount of chromium, which is very toxic and carcinogenic. In other ways, treating wastewaters cost the industries large amount of money. Therefore, the aim of this research is to remove chromium from tannery wastewater by adsorption using activated carbon prepared from locally available and low-cost plants known as parthenium under factorial study design of $2^4$ (16 runs, the combinations of four independent variables).*

*Factorial study design is known for its simplicity, cost-effectiveness, less time consuming, and to interaction among variables. In this factorial study, four independent variables such as, pH, time, initial concentration, and adsorbent dosage, and one dependent variable, removal efficiency were considered. For optimization purpose, the synthetic tannery wastewater was prepared in the laboratory. The characterization of activated carbon developed from parthenium stem such as; Proximate analysis, scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and surface area determination were performed.*

*The results of adsorption tests done on synthetic wastewater showed that the prepared activated carbon was able to remove 90.54 % of chromium from wastewater at pH 2, Contact time of 90 minutes, adsorbent dosage of 10 g/110ml solution, and initial chromium concentration of 100mg/L. After optimization the test was repeated on the actual tannery wastewater and the removal efficiency of the adsorbent was 89% which proved activated carbon prepared from parthenium stem can be used to treat the wastewater of the leather tanning industrial sector.*

*Finally, the treatment system was tested by two well know isothermal models in water and wastewater treatment system, Langmuir Freundlich isotherms. And the Freundlich isotherm was best fitted with the experimental data.*


***Key words:*** adsorption, parthenium stem, adsorption isotherms.

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## List of Abbreviations, Acronyms and Symbols

AC: Activated carbon

ANOVA: Analysis of variance

APHA: American Public Health Association

ASTM: American Society for Testing and Materials

$BOD_5$: Five days biochemical oxygen demand

COD: Chemical oxygen demand

EC: Electrical conductivity

EPA: Environmental Protection Authority

FTIR: Fourier transform infrared spectroscopy

PAC: parthenium activated carbon

SEM: scanning electron Microscope

TDS: Total dissolved solids

TS: Total solids

TSS: Total suspended solids

# CHAPTER ONE

# 1. INTRODUCTION

In this chapter, 6 topics were discussed. These included back ground of study which focused on the problem of heavy metals released to environment through leather tanning industry and heavy metals removal from wastewater by adsorption. The availability and potentials of specified plant as adsorbent was discussed as well. Objectives of the study, research questions answered by this study, scope and significance of the study was also briefly discussed.

## 1.1. Background of study

Heavy metals contamination is a growing issue affecting living organisms throughout the world (Khamis, Jumean, and Abdo 2009; Song et al. 2016). Due to the fast development of industrial facilities, direct and indirect discharges of heavy metals to the environment through wastewater have tremendously been increased (Khamis et al. 2009). Some studies indicated that, in industrial wastewater treatment; chromium, copper, cadmium, lead, zinc and nickel are considered more toxic and receiving more attentions (Fu and Wang 2011).

Chromium (Cr) is a harmful heavy metal and exists in various oxidative forms; however, the trivalent and hexavalent states are considered more essential in term of environmental pollution point of view (Goyal, Jain, and Banerjee 2003). It is considered more harmful and toxic due to its high carcinogenic and resistant properties. In many countries, concentration of Cr (VI) is severely restricted and as per American Environmental Protection Agency (EPA) guidelines the maximum permitted limit for Cr (VI) in inland surface, potable and industrial wastewaters are 0.1, 0.05, and 0.25 mg/L, respectively. Over ingestion of Cr beyond the permissible limits (1,000 microgram perday) can cause severe

gastric damage, liver, kidney and lung cancer and other health related complications (Patel 2011a). There are varied Cr contamination sources such as electroplating, leather tanning, textile industries, metal finishing, nuclear power plants, and chromate preparation (Suhada et al. 2013).

Leather tanning is the process which converts the raw hide into a stable material which is suitable for wide variety of end applications. There are many methods and materials in tanning process which ultimately depend on the end application of the leather. The commonly used tanning material now a days is chromium that leaves the leather a pale blue color due to the chemical. This process uses high amount of water that can lead to the production of high amount of wastewater. According to Gupta & Parmeggiani, 2003, the production of one tonne of hide/skin generally produces 20 to 80 $m^3$ of turbid and foul-smelling wastewater, including chromium levels of 100-400mg/L, sulfides levels from 200 to 800 mg/L, nitrogen levels from 200 to 1,000mg/L, $BOD_5$ levels from 900 to 6,000 mg/L, COD levels from 800 to 43,000 mg/L and high levels of fat (Gupta and Parmeggiani 2003).

Although rapid industrial expansion in Ethiopia is viewed as an indicator of economic progress, they are greatly associated with environmental degradation, particularly due to the discharge of untreated or partially treated wastewater. Leather tanning has been ranked as one of the most polluting activities in Ethiopia due to the high growth rate and discharge of untreated wastewater to the environment. At present there are more than thirty-one tanning industries in Ethiopia, operating fully (LIDI, 2013). Only a few of the industries in Ethiopia have the treatment facilities and can treat their wastewaters to any degree, while most of them discharge their wastewater into nearby water bodies and open land without any form of treatment (Tadesse and Seyoum 2015). Hence, discharge of tannery waste

water into the environment pose severe threat in aquatic plants, animals and human health due to their toxicity, high oxygen demanding, eutrophication and persistence in the environment (Doble, Kumar, and Pruden 2006). So, there should be a significant management of wastewater from leather tanning industries before it released to environment.

However, there are different methods of chromium removal from wastewater including chemical precipitation, filtration, chemical oxidation and reduction, reverse osmosis, evaporation, electrochemical and ion exchange, still these methods subjected to high costs, complex technology, problems of sludge handling, large surface area, and long detention period (Brozou et al. 2013; Khamis et al. 2009). So, attentions must be given to focus on low cost and locally available materials to remove this pollutant from wastewater by adsorption.

Adsorption is newly developed technology effective for pollutant removal using locally available low-cost materials. Several studies have been performed to remove chromium from wastewater using adsorbents developed from rice hull (Chen et al., 2018), henna leaves, chufa corm peels, peel of banana, wheat bran, etc. (Memon et al. 2008; Shanthi and Selvarajan 2012; Singh et al. 2008). However, these adsorbents have relatively low adsorption capacity to Cr, therefore, it is necessary to search for highly abundant naturally available, low cost and greater adsorption capacity adsorbent in order to alleviate Chromium from contaminated water. Accordingly, in this study adsorbents prepared from Parthenium hysterophorus stem was used.

Parthenium hysterophorus is species of flowering plant native to American tropics. Its

common name includes Santa-Maria, white top weed, and famine weed. Due to its high growth rate and adaptability to various environmental conditions, it spreads to cover larger area in short time (Bapat and Jaspal 2016). Recent studies on this plant have found numerous uses. Among them, as remedy for skin inflammation, rheumatic pain, diarrhea, urinary track infections, malaria and neuralgia (Patel 2011b). The other potential uses of parthenium hysterophorus is being investigated as a means of removing heavy metals and dyes from wastewater (Kadirvelu et al. 2002).

### 1.2. Statement of the problem

Tannery industry is one of the most polluting industrial sectors (Landgrave 1995). Almost every tannery industry uses significant amount of chemicals in the process of transforming animal skin in to leather (Chowdhury et al. 2015). Chromium is one of the most commonly used tanning chemical in tannery industry (Bapat and Jaspal 2016). This process creates high volume of wastewater which are characterized by the high biological oxygen demand (BOD), high chemical oxygen demand (COD) and high concentrations of suspended solids, organic nitrogen, sulphide and chromium (Gutterres et al. 2015). In another ways, the treatment of the wastewaters in conventional methods forces industries to invest high amount of money, time and human power. Since industries work for profit, they are not willing to invest on their waste treatment and many industries are releasing their wastewater directly to environment without proper treatment. This practice is common in developing countries like Ethiopia.

Ethiopia is under rapid growth of industries and towns, some liquid wastes containing high concentration of toxic elements from old as well as new factories, is being released into water bodies without proper treatment (Minbale Aschale, Yilma Sileshi 2015). These

practices are one of the main causes of soil and water contamination and consequently cause of public health problem (Fu and Wang 2011). So, there should be a method to treat wastewater with low-cost using locally available materials with high pollutant removal efficiency. One of the newly technologies developed for treating wastewater at low-cost is adsorption.

Expansion of tannery industries in Ethiopia and discharge of untreated or partially treated tannery wastewater to the water bodies pose greater health risks to the downstream users and ecological degradation in water bodies (Alemu 2017). Many people living around the river where tannery industries constructed could face shortages of clean water and many of them are depending on Lake and river water for a variety of purposes such as drinking, fishing, livestock watering, irrigation, and recreation. Due complex composition of tanning industry wastewater, providing adequate wastewater treatment to meet Ethiopian EPA discharge limits becomes a challenge. Effluents from the existing conventional treatment systems often contain contaminants of a certain residual concentration, which cannot meet EPA allowable discharge limits. The problem has now forced the Ethiopian government to set discharge limit standards which demand the industries to treat their wastewater. The government also forces the industry owners to build a treatment system that can treat the pollutants that can meet permissible limits. This calls up the development of efficient and integrated treatment methods. In Ethiopia only, few treatment technologies have been practiced for the treatment of tannery wastewater. The most common are oxidation pond, primary and a combination of primary and secondary treatment system (Tadesse and Guya 2017). In addition, the performance data for the existing wastewater treatment systems was not available.

### 1.3. Research Questions

The following research questions were addressed by this study.

1. What are the characteristics of adsorbent prepared from parthenium hysterophorus stem?
2. What is the efficiency of activated carbon prepared from parthenium hysterophorus stem in removing chromium from synthetic tannery wastewater?
3. What is the adsorption isotherm of the treatment system?

### 1.4. Objective

#### 1.4.1. General Objective

The main objective of this study was to investigate the adsorption capacity and mechanisms of chromium removal from synthetic tannery wastewater using activated carbon developed from Parthenium hysterophorus stem under factorial experimental treatment system.

#### 1.4.2. Specific objectives

- To develop and characterize Activated carbon adsorbent from parthenium hysterophorus stem
- To determine the adsorption performance of activated carbon developed from parthenium stem in removal of Chromium from synthetic tannery wastewater under factorial experimental design
- To determine factors affecting adsorption (time, pH, dose, and initial concentration)
- To evaluate the adsorption isotherms of the treatment system

### 1.5. Significance of study

This study can give a great advantage for developing countries which have low income and can't access high technology to remove heavy metals from industrial wastewater. It alarms

them to use locally available materials with low cost to remove chromium from wastewater and meet permissible guide lines to release wastewater into environment. Specially, for tropical and sub-tropical countries, where parthenium hysterophorus is abundantly found, it gives a good information to use as input for further study to develop chromium removal technology from tannery wastewater.

Ethiopia is country with accelerated economic growth and industrial park establishments. These industries generate a significance amount of wastewater. This research can give a key to use activated carbon developed from parthenium stem which is locally available to remove total chromium from wastewater.

### 1.6. Scope of the study

This study was based on laboratory experiment to remove chromium from synthetic tannery wastewater using activated carbon prepared from parthenium stem. The optimization of the treatment system was done using four independent variables; contact time, pH, adsorbent dose, and Chromium concentration while the removal efficiency of adsorbent was dependent variable. This study covers the preparation and characterization of adsorbent from parthenium stem as well as the preparation of synthetic tannery wastewater in the laboratory. The research was focused on the removal of chromium from tannery wastewater. Finally, actual tannery wastewater characterization and the removal efficiency of the adsorbent was tested using maximum removal values of variables.

# CHAPTER TWO

# 2. LITERATURE REVIEW

The literature review part of this research was focused on; The background of leather tanning industries, the process in leather productions, the water and wastewater of tannery industries, wastewater treatment methods in tanneries, adsorption and adsorbent preparation methods, adsorption isotherms, and the potential of parthenium plant as an adsorbent. Each section was described in detail and in line with the objectives and methodology of the research.

## 2.1. Leather Tanning Industry

Tannery is a place where raw hides and skins are converted in to leather by applying tannin or tannic acid. This process of tanning has been appropriately referred to a series of baths in water containing certain ingredients (Belay 2010). Tanning is an art by which putrescible animal hides and skins are preserved from decay and converted into non-perishable substance, known as Leather. Man has been aware of this art since the dawn of human civilization. Many ancient civilizations had evolved and perfected this art of making leather. The earliest records of such ancient civilization, those of Egypt, and China, establish the fact that the art was well-known to the ancient people and was widely practiced. According to historians, the art of the tanning originated before the dawn of recorded history. Tanning has two types of processes, such as Vegetable Tanning (where vegetable tanning materials are employed); and Chrome Tanning (where the basic chromate is used). Earlier, Vegetable tanning was in operation; but today, almost all the tanneries process their leather through Chrome tanning to reduce time and to produce quality leather (Basaran, Bitlisli, and Aslan 2008; Landgrave 1995).

The vegetable tanning was comparatively harmless. This process is time-consuming taking 40 - 45 days to change from skin to finished leather. With the increase in demand for finished leather in the world market, most of the tanneries have turned to Chrome Tanning. In this process, various chemicals, fat liquor oil and dyes are used. The raw skins and hides are received in the tanneries in wet salted or dry salted form. The salt (Sodium Chloride) is used as a preservative and is first removed and then skins and hides are put into various processes, like Soaking, Liming, Airing, Fleshing and De-liming, followed by washing and tanning (Basaran et al. 2008).

### 2.1.1. Leather Production Process

The leather manufacturing process is divided into three sub-processes: *preparatory stages, tanning and crusting.* All true leathers undergo these sub-processes. A further sub-process, surface coating may be added into the sequence. The list of operations that leathers undergo vary with the type of leather. The preparatory stages are when the hide/skin is prepared for tanning. During the preparatory stages many of the unwanted raw skin components are removed. Many options for pretreatment of the skin exist. Not all the options may be performed. Preparatory stages may include: Preservation, soaking, liming, unhairing, fleshing, splitting, bating, degreasing, frizzing, bleaching, pickling, depickling - raising of the pH out of the acidic region to assist with penetration of certain tanning agents (Zeiner et al. 2011).

Through tanning the protein of the raw hide or skin is converted into a stable material which is suitable for a wide variety of end applications. The principal difference between raw hides and tanned hides is that raw hides dry out to form a hard-inflexible material that can putrefy when re-wetted (wetted back), while tanned material dries out to a flexible form

that does not become putrid when wetted back. Many different tanning methods and materials can be used; the choice is ultimately dependent on the end application of the leather. The most commonly used tanning material is chromium, which leaves the leather, once tanned, a pale blue color (due to the chromium), this product is commonly called (Cassano et al. 1997). The acidity of hides once they have finished pickling will typically be between pH of 2.8-3.2. At this point the hides are loaded in a drum and immersed in a float containing the tanning liquor. The hides can soak, and the tanning liquor slowly penetrates through the full substance of the hide. Regular checks will be made to see the penetration by cutting the cross section of a hide and observing the degree of penetration. Once an even degree of penetration is observed, the pH of the float is slowly raised in a process called basification. This basification process fixes the tanning material to the leather, and the more tanning material fixed, the higher the hydrothermal stability and increased shrinkage temperature resistance of the leather. The pH of the leather when chrome tanned would typically finish somewhere between 3.8-4.2 (Sharphouse 1983).

Another leather production sub-process is crusting. Crusting is when the hide/skin is thinned, retanned and lubricated. Often a coloring operation is included in the crusting sub-process. The chemicals added during crusting must be fixed in place. The culmination of the crusting sub-process is the drying and softening operations. Crusting may include; wetting back, summing, splitting, shaving, neutralization, retanning, dyeing, fat liquoring, filling, stuffing, stripping, whitening, fixation, setting, drying, conditioning, softening, buffing (Heidemann 1993).

### 2.1.2. Leather tanning industry water and wastewater

Leather processing involves a huge amount of water in its different stages and therefore it

produces a considerable amount of wastewater, which demands high investments and operational cost for effluent treatment to satisfy the discharge standards required by environmental legislation. Nearly 40-45 L water/kg raw-hide is used by tanneries for processing finished leathers. With annual raw-hide or skin processing of the order of 690,000 tones, total water requirements for the industry approximate 30 billion liters. Such huge volume of water, used in leather processing, poses problems such as, availability of water in required quantity and the treatment of generated wastewater (Sundar et al. 2001).

One tone of hide or skin generally leads to the production of 20 to 80 m3 of turbid and foul-smelling wastewater, including chromium levels of 100–400 mg/L, sulfide levels of 200–800 mg/L and high levels of fat and other solid wastes, as well as notable pathogen contamination. Pesticides are also often added for hide conservation during transport. With solid wastes representing up to 70% of the wet weight of the original hides, the tanning process comes at a considerable strain on water treatment installations In addition to the other environmental impacts of leather, the production processes have a high environmental impact, most notably due to: The heavy use of polluting chemicals in the tanning process and air pollution due to the transformation process (Ludvík 2000).

### 2.2. Industrial wastewater treatment methods

There are many types of industrial wastewater. Based on different industries and contaminants; each sector produces its own combination of pollutants. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced (APHA 1998; Gutterres et al. 2015). The most commonly used industrial wastewater treatment methods are biological and physicochemical wastewater treatment methods.

### 2.2.1. Biological wastewater treatment method

In biological wastewater treatment, the wastewater is introduced into a specially designed bioreactor where under aerobic or anaerobic conditions the organic matter is utilized by microorganisms such as bacteria (aerobically or anaerobically), algae, and fungi (aerobically). The bioreactor affords appropriate bioenvironmental conditions for the microorganisms such as, oxygen and food, in the form of settled wastewater, are supplied to the microorganisms, the biological oxidation process of dissolved organic matter will be maintained (Samer 2015).

The biological process is mostly carried out by bacteria that form the basic trophic level (the level of an organism is the position it occupies in a food chain) of the food chain inside the bioreactor. The bioconversion of dissolved organic matter into thick bacterial biomass can fundamentally purify the wastewater (Samer 2015).

The principles of biological treatment of wastewater are stated in summary as follows

i. The biological systems are very sensitive for extreme variations in hydraulic loads.
ii. The growth rate of microorganisms is highly dependent on temperature and pH.
iii. BOD is efficiently treated in the range of 60 to 500 mg L-1. Wastewaters in excess of 500 mg L-1 BODs have been treated successfully if enough dilution is applied in the treatment process.
iv. The biological treatment is effective in removing up to 95% of the BOD. Large tanks are required in order to eliminate the entire BOD, which is not feasible.
v. The biological treatment systems are unable to handle “shock loads” efficiently. Equalization is necessary if the variation in strength of the wastewater is more than 150% or if that wastewater at its peak concentration is in excess of 1,000 mg L-1

BOD (Jahan et al. 2015).

vi. The carbon: nitrogen: phosphorus (C: N: P) ratio of wastewater is usually ideal. The C: N:P ratio of industrial wastewaters should range from 100:20:1 to 100:5:1 for a most advantageous biological process (Natarajan et al. 2013).

vii. If the C: N:P ratio of the wastewater is strong in an element in comparison to the other elements, then poor treatment will result. This is especially true if the wastewater is very strong in carbon. The wastewater should also be neither very weak nor very strong in an element; although very weak is acceptable, it is difficult to treat.

viii. Oils and solids cannot be handled in a biological treatment system because they negatively affect the treatment process. These wastes should be pretreated to remove solids and oils.

ix. Toxic and biological-resistant materials require special consideration and may require pretreatment before being introduced into a biological treatment system.

x. Although the capacity of the wastewater to utilize oxygen is unlimited, the capacity of any aeration system is limited in terms of oxygen transfer.

### 2.2.2. Physicochemical wastewater treatment methods

Physicochemical treatment involves using chemicals which can modify physical state of colloidal particles which helps in making them more stable and coagulable for further treatment or filtration purposes. This treatment methods have been used for over a century in conjunction with biological treatment methods. These methods have been successfully used for industrial water treatment, conditioning of wastewater sludge as part of pre-treatment with increasingly higher efficiency and decreasing costs. Physicochemical

treatment can have considerable influence on biodegradation potential of organic material in the wastewater (Anon 2014; Supriya, Palanisamy, and Shanthi 2014).

Overall performance of physicochemical treatment process can depend on several aspects and physicochemical properties of waste water. Therefore, laboratory tests are routinely conducted to determine properties based on which the overall treatment process can be customized in terms of times, types and dosage of chemicals etc. (Fersi et al. 2018). Among physicochemical wastewater treatment methods adsorption is one of the newly developed technology effectives in removing contaminants from the wastewater.

Adsorption is a physical process where adsorbates are removed by attachment to the surface of a solid substrate (adsorbent). Adsorbents should have an extremely high specific surface area. Examples of widely used adsorbents include activated alumina, clay colloids, hydroxides, resins, and activated carbon. Therefore, the adsorbent should be activated before use. A wide range of organic materials can be removed by adsorption, including detergents and toxic compounds (Czelej et al. 2016). The adsorption capacity ($q_e$), one of the most important characteristics of an adsorbent, can be calculated as follows:

$$\text{Adsorption Capacity}\left(\frac{\text{mg}}{\text{g}}\right) = \frac{\text{Adsorbate}}{\text{Adsorbent}}$$

The adsorption process can be affected by different factors. Among them, the mains are the following;

- Particle diameter: the adsorption is inversely proportional to the particle size of the adsorbent, and directly proportional to surface area.
- Adsorbate concentration: the adsorption is directly proportional to adsorbate concentration.

- Temperature: the adsorption is directly proportional to temperature.
- pH: the adsorption is inversely proportional to pH due to surface charge.

The natures of adsorption processes can be either exothermic or endothermic which depends on the adsorption thermodynamics. The endothermic adsorption process is enhanced by increasing the temperature, whereas the exothermic adsorption will be favored at decreasing temperature. Normally, the increase of contact time will increase the uptake capacity of adsorbent to a certain point before it becomes constant. However, the pH of the solution affects the surface charge of the adsorbent, and the degree of ionization of the materials present in the solution and speciation of the adsorbate. This phenomenon can result in shifting the reaction kinetics and equilibrium characteristics of adsorption process.

The most widely used adsorbent is activated carbon, which can be produced by pyrolytic carbonization of biomass. Activated carbon is the most implemented adsorbent and is a sort of carbon processed to be riddled with small, low-volume pores that enlarge the surface area available for adsorption (Das, Samal, and BC 2015). Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. Activated carbon can be manufactured from carbonaceous material, including coal, peat, wood, or nutshells. The manufacturing process consists of two phases, carbonization and activation ( Anon 2013). The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons from the raw material, as well as to drive off any gases generated. The process is completed by heating the material over 400 °C (750 °F) in an oxygen-free atmosphere that cannot support combustion (Belgacem et al. 2013).

Due to its high degree of micro porosity, one gram of activated carbon has a surface area in excess of 3,000 $m^2$ as determined by gas adsorption (Dillon et al. 1989). An activation level enough for useful application may be obtained solely from high surface area. Further chemical treatment often enhances adsorption properties (Naeem et al. 2016).

**Activated carbon preparation methods**

Activated carbon is carbon produced from carbonaceous source materials such as bamboo, coconut husk, willow peat, wood, coir, lignite, coal, and petroleum pitch. It can be produced by one of the following processes:

I. **Physical activation:** The source material is developed into activated carbons using hot gases. Air is then introduced to burn out the gasses, creating a graded, screened and de-dusted form of activated carbon. This is generally done by using one or a combination of the following processes:

   - ✓ **Carbonization:** Material with carbon content is pyrolyzed at temperatures in the range 600–900 °C, usually in inert atmosphere with gases like argon or nitrogen
   - ✓ **Activation/Oxidation:** Raw material or carbonized material is exposed to oxidizing atmospheres (oxygen or steam) at temperatures above 250 °C, usually in the temperature range of 600–1200 °C.

II. **Chemical activation:** Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (Romanos et al. 2012) (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride ). Then, the raw material is carbonized at lower temperatures (450–900 °C). It is believed that the carbonization / activation step proceeds simultaneously

with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

Activated carbons are complex products which are difficult to classify based on their behavior, surface characteristics and other fundamental criteria. However, some broad classification is made for general purpose based on their size, preparation methods, and industrial applications (Diao, Walawender, and Fan 2002; Zubrik et al. 2017).

Natural materials which are available in large quantities, or certain waste products from industries or agricultural operations, may have potential as inexpensive adsorbents. Generally, an adsorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course, improved adsorption capacity may compensate the cost of additional processing. Research has already been conducted on a wide variety of adsorbents. They include walnut shell, waste tea, Turkish coffee, nut shell, exhausted, saw- dust, rice bran, soya bean and cotton seed hulls, peat, sorghum, and peanut hull carbon have been investigated to remove nickel (II) from wastewater. Reports have appeared on preparation of activated carbon from biomass like soya bean, peanut, pecan and walnut shells (Z. Al-Qodah and R. Shawabkah 2006). In this study the activated carbon prepared from Parthenium stem was used.

Cost- effective alternative technologies or absorbents are needed for the treatment of metal contaminated wastewaters especially in developing countries. Lata et al. (2008) studied the adsorption capacity of Parthenium hysterophorus for the removal of nickel from aqueous solution by varying parameters such as agitation time (Bapat and Jaspal 2016; Singh et al. 2008). This Sulphuric acid treated carbonized Parthenium could be an effective, easily

available and low-cost adsorbent for the removal of Ni (II) from dilute aqueous solution. In other ways, Ajmal et al. (2006) studied the efficiency of dried powder of Parthenium hysterophorus as an adsorbent for removing Cd (II) from waste water. Batch process was employed for adsorption of Cd (II) ions by dried and crushed mass of Parthenium hysterophorus. According to author, Atomic absorption spectrophotometry of the filtrate showed that Partehnium hysterophorus is an effective adsorbent over a wide range of initial Cd (II) concentration. The maximum adsorption of Cd (II) ions in the pH range 3–4 was 99.7%. The desorption studies showed 82% recovery of Cd (II) from the adsorbent.

In another study, adsorbents prepared from Parthenium hysterophorus are tested to remove methylene blue from an aqueous solution in a batch reactor. Dye adsorption capacity of sulphuric acid treated parthenium and phosphoric acid treated parthenium is compared with that of commercially available activated carbon. Maximum dye is sequestered by commercial activated carbon; however, sulphuric and phosphoric treated parthenium activated carbon also showed significant results and can be considered as potential adsorbents for methylene blue removal from dilute aqueous solutions (Lata et al. 2007). Going by these promising findings, this weed can be exploited for industrial pollution control.

**2.3. Adsorption isotherms**

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent at constant temperature (Czelej et al. 2016; Foo and Hameed 2010). With use of Isotherm, which can provide fundamental physicochemical data to evaluate the adsorption capacity, it is possible to select suitable adsorbent. The isotherm also provides additional information

to evaluate the affinity of an adsorbate by the adsorbent. Furthermore, adsorption isotherm described by many theoretical and empirical models has been developed to represent the mechanism and shape of adsorption process. Generally, the knowledge of adsorption equilibrium is helpful to understand the mechanism of an adsorption process and to describe the interaction between the adsorbate and adsorbent.

$$Adsorbate + Adsorbent \xrightarrow{\text{Adsorption}} Adsorption$$

There are several types of equilibrium isotherm equations which describe the adsorption equilibrium characteristics. Langmuir and Freundlich equations are examples of such models that are commonly used to describe adsorption isotherms in water and wastewater treatment applications.

### 2.3.1. Langmuir isotherm

In 1916 Langmuir proposed Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identified sites. The theoretical Langmuir isotherm as one of the most traditional models has a maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent. The general form of Langmuir isotherm model is given by the following formula.

$$q_e = \frac{q_{\max} \mathrm{KlC}_e}{1 + \mathrm{KlC}_e}$$

While the linearized form of Langmuir isotherm is given using the following formula.

$$\frac{Ce}{qe} + \frac{1}{qmax} Ce + \frac{1}{KLqmax}$$

Where $C_e$ is the equilibrium concentration of solute in solution (mg/L), $q_e$ is the equilibrium

concentration on the adsorbent (mg/g), $K_L$ the Langmuir constants (L/mg) related to the free energy of adsorption, and $q_{max}$ the maximum monolayer adsorption capacity of the adsorbent (mg/g) (Chen et al., 2013; Gandhi et al., 2014). And also, the value of $q_e$ can be calculated from the following equation.

$$qe = \frac{Co - Ce}{m} V$$

where $C_o$ (mg/L) is initial concentration of adsorbate and $C_e$ (mg/L) is concentration of adsorbate at equilibrium whereas V (L) is the volume of the adsorbate and m is the mass of the adsorbent in g. In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter ($R_L$)

$$R_L = \frac{1}{1+KLC_0}$$

Where, $K_L$ (L/mg) is the Langmuir isotherm constant and $C_o$ (mg /L) is the initial concentration of adsorbate. There are four probabilities for the $R_L$ value: For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$ (Foo and Hameed 2010).

### 2.3.2. Freundlich Isotherm model

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm. This model is suitable for heterogeneous surfaces with non-uniform distribution over the adsorbent. The Freundlich isotherm equation assuming that the adsorption takes place on heterogeneous surfaces of solids and in a multilayer

sorption manner. This isotherm, Freundlich isotherm model, is given by the following formulas.

$$q_e = K_F \mathrm{Ce}^{1/\mathrm{n}}$$

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} Log\ C_e$$

$K_F$ indicates adsorption capacity (mg/g) and 1/n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The plot of log $qe$ versus log $Ce$ is employed to generate $K_F$ value from the intercept and n value from the slop. The characteristics of the Freundlich isotherm are expressed in terms of intensity of the adsorption process (n). The results using this variable allow evaluating if a chemical ($n < 1$) or physical ($n > 1$) adsorption. For values in the range $0 < 1/n < 1$, adsorption is favorable. The greater the values of $K_F$ better is the favorability of adsorption (Attar 2010).

### 2.4. Ethiopian Tanneries and their wastewater management practices

Tanning industry in Ethiopia is currently believed to be one of the sectors supporting economic development of the country significantly by generating foreign currency and it is also pollutant intensive sector that threatens the environment at large. Ethiopian tanneries are now on a new path of adding values to the products that therefore requires a series of additional individual process steps and varieties of chemical input that possibly intensifies the pollution load of the waste water effluent. The environment and development integration in a leather industry has to be strengthened to achieve the intended sustainable economic benefit for human wellbeing (Patrice et al. 2008; Tadesse and Guya 2017). Tannery waste water effluent is treated in many different ways. In Ethiopia there are situations in which tanneries treat their wastewater partially (Alubel Abtew 2015).

According to Ethiopian leather Industry Development Institute (LIDI) data, currently there are 27 leather tanning industries, 42 Leather product industries, 19 Foot wear industries, and 4 glove industries functioning in different parts of the country (LIDI 2019). The institute (LIDI) also gives different services for the industries such as giving laboratory testing for water and wastewater, physical Testing on Leather, physical Testing on Footwear, and Leather Chemical & Eco-Chemical Analysis for the industries.

# CHAPTER THREE

# 3. MATERIALS AND METHODS

In this chapter; the methods of study, sample collection methods, the materials used, study area and periods, adsorbent preparation and characterization, details of used isothermal models as well as data analysis and presentation methods were included.

## 3.1. General description of the study site

A tannery wastewater sample was collected from Gellan Tannery PLC wastewater equalization tank. Gellan Tannery is a private limited company established in 2006. It is located in Oromia's Industrial city, Modjo, 70 km from Addis Ababa. At present the factory processes over 4000 pieces of sheep skins and 1500 pieces of goat skins per day.


Figure 1. Google image of Gellan Tannery location.

### 3. 2. Study Design

In this research, laboratory based experimental study design was conducted in Addis Ababa Science and Technology University, Addis Ababa city, Ethiopia. Sample Analyses were performed at the laboratories of Ethiopian Leather Development Institute, Addis Ababa University, and Addis Ababa Science and Technology University. The study was conducted from September 2018 to mid-January 2019. Parthenium stem sample was collected and taken to laboratory and air dried at room temperature. After all important preparation and characterization of sample, the powder of sample was ready for synthetic laboratory test. The next step was preparing synthetic leather tanning wastewater which consists of most of tannery wastewater impurities. Finally, real waste water was taken from Gellan Tannery PLC and the removal efficiency of adsorbent was checked.

### 3. 3. Study variables

In this study, there were four independent variables. These were, pH, contact time, Initial chromium concentration, and Adsorbent dose while the dependent variable was Chromium adsorption capacity of activated carbon prepared from parthenium stem.

### 3.4. Preparation of synthetic leather tanning wastewater

Leather tanning industries wastewater is mainly characterized by high amount of BOD, COD, TDS, chromium and other metallic ions (CHEMIASOF 2011; Jahan et al. 2015). The synthetic wastewater prepared in the laboratory was prepared in a way it represents actual tannery wastewater. The synthetic tannery wastewaters were prepared in 16 different conical flasks of 500ml. In all conical flasks (16) the solutions prepared from analytical reagents which composed of 4.9 mg/L of copper, 3.2 mg/L of Lead, 7.4 mg/l of Zinc, 40 mg/L of calcium, 15 mg/L of Potassium, and 150 mg/L of sodium ions were added. And 1000 mg/L of chromium solution was prepared from 2.825 g of Potassium dichromate

dissolved in 1 L of distilled water from which Synthetic samples of different concentrations of Cr (40mg/L and 100mg/l) were prepared from this stock solution by appropriate dilution

Figure 2. Synthetic tannery wastewater during preparation

according to the initial concentrations required for the optimization process and the pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions (Song *et al.*, 2016).

### 3.5. Materials used

Among many materials and equipment's used in this study, the majors were: Fourier transform infrared spectroscopy, Scanning electron microscope (Inspecto F50), incubator orbital shaker, muffle furnace, oven, UV-visible spectrophotometer (Optizen pop), pH and temperature meter.

### 3.6. Adsorbent preparation and characterization

In this portion, the details of how activated carbon was prepared from parthenium stem was discussed. Moreover, the characterization of prepared adsorbent was described in detail.

#### 3.6.1. Adsorbent preparation

Parthenium hysterophorus stem sample was collected from Addis Ababa science and technology University compound. The collected Parthenium hysterophorus stem was taken

to laboratory and washed with tap water to remove dust and was dried at room temperature for three weeks.

The dried parthenium stem was grinded to reduce the size.


Figure 3. (a) Parthenium stem during collection and (b) dried parthenium ready for crushing.

The grinded sample was activated using phosphoric acid solution (50%). Phosphoric acid is widely used as an activating agent in the preparation of activated carbons because of its advantages such as its non-polluting character compared to zinc chloride and its ease of elimination by leaching with water, with the recovered phosphoric acid being recycled for further use (Shu et al. 2017). The ratio of parthenium sample to acid was 1:1 (weight of parthenium stem sample in gram to volume of acid in ml). The impregnation was kept for 24 hours for proper soaking at room temperature followed by drying for 24 hours at 105 $^{o}$C in incubator. Afterwards the sample was pyrolyzed in furnace at 500 °C for 2 hours. After cooling in desiccator, the sample was washed with deionized distilled water until the pH of the adsorbent reached ~7:00.

Figure 4.The crushed parthenium stem during impregnation and after impregnation

### 3.6.2. Adsorbent characterization

After the preparation of activated carbon, the next step was characterizing it to know the details about the carbon which discussed in detail in this sub topics. Characterization of activated carbon can tell if the specified materials are recommended for adsorbent development or not. Accordingly, proximate analysis (calculated directly), particle size determination (using test seive), surface area determination using iodine number, scanning electron microscope analysis (using Inspecto F50), and Fourier Transform infrared spectroscopy analysis were performed as characterization of adsorbent.

#### 3.6.2.1. Proximate analysis

Proximate analysis of activated carbon prepared from Parthenium hysterophorus stem was done as per standard methods of American Society for Testing and Materials (ASTM) to identify the amount of fixed carbon and non-carbon sources in the adsorbent. The moisture content was calculated by weighting 1.00g of sample and dried in incubator at 110 $^{o}$C for 3 hours and cooled in desiccator in the presence of drying agent and the difference between the initial weight of sample and final weight was calculated (Anisuzzaman et al. 2015).

$$Moisture\ content(\%) = \frac{Initial\ Weight\ -dried\ weight}{Initial\ weight} X\ 100\%$$

And for Ash content determination, 1 g of activated carbon prepared from parthenium stem was transferred to pre heated and dried crucible and burnt in furnace at 500 $^{o}$C for 4 hours. Finally, it was cooled to room temperature in desiccator in the presence of drying agents and weighted. Ash content of the sample was determined using the following equation (Nwabanne, J.T and Igbokwe 2012).

$$Ash\ content(\%) = \frac{Weight\ of\ ash}{Initial\ weight\ of\ sample} X\ 100\%$$

For the determination of volatile content of activated carbon prepared from parthenium stem, 1 g of sample was put in to pre-dried crucible of known weight and heated muffle furnace and heated at 900 $^{0}$C for 10 minutes (Nwabanne, J.T and Igbokwe 2012) and calculated using the following formula.

$$Vc\ (\%) = \frac{Weight\ of\ sample - weight\ sample\ after\ drying}{weight\ of\ sample} X\ 100\%$$

The percentage of fixed carbon was calculated from the difference of initial weight of sample and the sum of weights of moisture content, ash content and volatile matter as indicated by the following formula.

$$Fc\ (\%) = 100 - (\text{Moisture } + \text{ash content} + \text{Volatile matter})$$

**3.6.2.2. Particle size determination**

The particle size of adsorbent (activated carbon developed from parthenium stem) was fixed based on literature (Singh et al. 2008). Accordingly, the particles of desired mesh size of 106 micrometer was sieved using test sieve (Test Sieve, 30.4100.03, Germany) and collected and kept in sealed bottles for study.

### 3.6.2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was performed to identify functional group of adsorbents before and after adsorption. For FTIR analysis of activated carbon prepared from parthenium hysterophorus stem, a small amount of powdered adsorbent sample was mixed with dry KBr in the ratio of 1:100 mg and ground. After pressure was applied, the sample was scanned over a wave length of 4,000 - 400/cm by attenuated total reflection FTIR and the results were presented in form of graphs.

### 3.6.2.4. Iodine number and internal surface area determination

The iodine number is used to measure the porosity of the activated carbon by adsorption of iodine from solution. Each 1.0 mg of iodine adsorbed is ideally considered to represent 1.0 $m^2$ of activated carbon internal surface area (Z. Al-Qodah and R. Shawabkah 2006). To determine the Iodine number of activated carbons prepared from parthenium stem, 1 g of dried activated carbon was weighted and transferred to a glass stoppered 250ml Erlenmeyer flask followed by addition of 5% HCL into the flask and swirling until the activated carbon was wetted. Then the flask was placed on hot plate and boiled for 30 seconds. After boiling, the solution was cooled at room temperature and 100 ml of 0.1 N iodine solution was added and shaked vigorously for 30 seconds and filtered by gravity through what man filter paper. After filtration, 50 ml of filtered solution was added in to another 250 ml Erlenmeyer flask and titrated with 0.10 N of sodium thiosulphate until the yellow colour disappeared. Finally, 1 ml of starch solution was added and again titrated until the blue colour was disappeared. The volume of thiosulphate used was recorded at the end.

### 3.6.2.5. Scanning electron microscope (SEM) analysis

SEM analysis was done to determine surface morphology of activated carbon prepared from parthenium stem before and after the adsorption to check the porosity of the adsorbent

at different resolutions. The sample was applied on carbon tape and the scanning was done as per standard operating procedures of the machine (Inspecto F50) which was operated at 1000X and 4,000X magnifications and 5.00KV (Supra and Robbins 2010).

### 3.7. Tannery wastewater sampling and characterization

Important physicochemical parameters analysis of actual tannery wastewater was performed both at the field and in laboratory using standard water and wastewater sampling and analyses methods (APHA 1998). The samples were collected using plastic sampling bottles which were disinfected and rinsed with deionized distilled water. Prior to analyses the samples were stored in the refrigerator at 4 degrees Celsius to protect the alteration of the sample. Using the wastewater sample and keeping all parameters at optimum and equilibrium, adsorption experiments were carried out. During analysis, the duplicate measurements were performed, and the average results were reported.

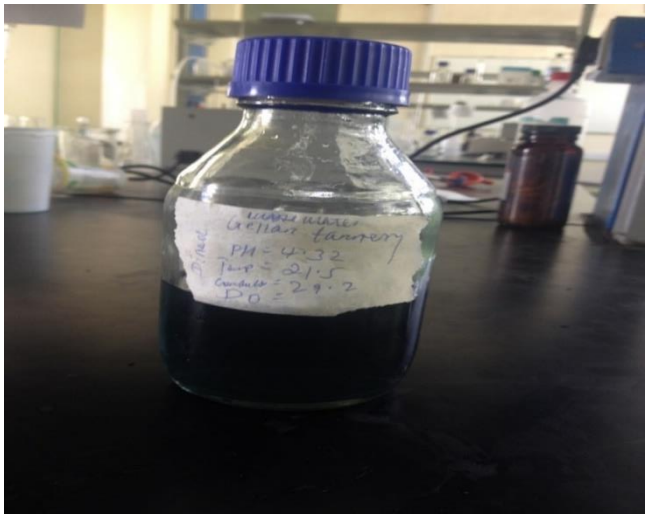

Figure 5. Tannery wastewater sample from Modjo tannery PLC.

#### 3.7.1. Characterization of tannery wastewater

The characterization of actual leather tannery industry wastewater was done both at onsite and in the laboratory. Multimeter apparatus was used for measurements of pH, temperature,

conductivity and dissolved oxygen on site. The others physicochemical analysis of the wastewater sample such as chemical oxygen demand (APHA 5220 B, Open reflux method), Total Dissolved Solid (APHA 2540 C, Total Dissolved Solids Dried at 180°C), Total Suspended Solid (APHA 2540 D, Total Suspended Solids Dried at 103–105°C), Total Solid ( APHA 2540 B, Total solid dried at 103 –105°C), and Biochemical Oxygen Demand of five days (APHA 5210 B, 5-days BOD test) were performed in the laboratory according to standard methods of water and wastewater analysis (APHA 1998; Chowdhury et al. 2015).

### 3.8. Adsorption experiments performance

The tests were carried out by adding 1 gram of activated carbon developed from parthenium stem of desired particle size (106 micrometer) containing 50 ml of potassium dichromate solution of known concentration (40 and 100 mg/L) and 10 ml of each interfering ions solutions into 500 mL conical flasks using 16 different combinations of the upper and lower values of the factors. Flasks were agitated at 125 rpm at 60 oC using incubated orbital shaker and the supernatant solution samples were waited for ten minutes to allow sedimentation of adsorbent in solution. Finally, the solutions were filtered using Whatman filter paper number 43. The filtrates were collected in different sampling bottles and Chromium removal efficiency was measured using optizen pop uv-visible spectrophotometer. Chromium removal efficiency was chosen as response variables. The experiments were performed in a random manner with the lower and higher values corresponding to (−) and (+), respectively. The levels of each factor was selected based on the literature values and target wastewater characteristics (Dhungana and Yadav 2009;

Singh et al. 2008; Siraj et al. 2012).

Figure 6. Prepared synthetic tannery wastewater during adsorption test

The level of each independent variables (pH, time in minutes, adsorbent dose in gram per volume of solution, Initial chromium concentration in mg/L) were indicated in table 1.

Table 1. Selected factors for factorial design

| **Selected factors for factorial design** | | |
|---|---|---|
| **Variables** | **Low (-)** | **High (+)** |
| pH | 2 | 6 |
| Time (minutes) | 45 | 90 |
| Adsorbent dose (g/110mL) | 1 | 10 |
| Cr Concentration (mg/ L) | 40 | 100 |

In other ways, the conical flasks were labeled with test numbers. Each test number represents the combination of all four variables as indicated in detail using table 2 below.

Table 2. Test number matrix of factorial design

| Test number | Chromium Conc, (mg/L) | pH | Time (minutes) | Adsorbent Dose (g/110mL) |
|---|---|---|---|---|
| **1** | 40 | 2 | 45 | 1 |
| **2** | 100 | 2 | 45 | 1 |
| **3** | 40 | 6 | 45 | 1 |
| **4** | 100 | 6 | 45 | 1 |
| **5** | 40 | 2 | 90 | 1 |
| **6** | 100 | 2 | 90 | 1 |
| **7** | 40 | 6 | 90 | 1 |
| **8** | 100 | 6 | 90 | 1 |
| **9** | 40 | 2 | 45 | 10 |
| **10** | 100 | 2 | 45 | 10 |
| **11** | 40 | +6 | 45 | 10 |
| **12** | 100 | 6 | 45 | 10 |
| **13** | 40 | 2 | 90 | 10 |
| **14** | 100 | 2 | 90 | 10 |
| **15** | 40 | 6 | 90 | 10 |
| **16** | 100 | 6 | 90 | 10 |

Finally, Adsorption removal efficiency of activated carbon was calculated using the following formula for each test number and the results were indicated in % removal.

$$\% R = \frac{Ci - Cf}{Ci} X\ 100\%$$

Where % R the removal percentage of chromium by activated carbon, $C_i$ initial concentration of chromium in solution (mg/L) and $C_f$ is final concentration of chromium after treatment (mg/L).

### 3.9. Adsorption isotherms

Adsorption Isotherms was used to evaluate the chromium adsorption capacity of activated carbon developed from parthenium stem, the relationship between the amount of chromium adsorbed at equilibrium per unit mass of the adsorbent and the concentration of chromium in the aqueous phase at equilibrium was analyzed by applying adsorption isotherm models. The two widely used isotherms models in water and wastewater treatment were Langmuir and Freundlich models. Accordingly, the results of this study were tested with these two isothermal models (Langmuir and Freundlich). The general form of Langmuir isotherm model is given as follow.

$$q_e = \frac{q_{\max} \mathrm{KLC}_e}{1 + \mathrm{KLC}_e}$$

While the linearized form of Langmuir isotherm was given using the following formula.

$$\frac{Ce}{qe} + \frac{1}{qmax} Ce + \frac{1}{KLqmax}$$

Where $C_e$ is the equilibrium concentration of solute in solution (mg/L), where $q_e$ is the equilibrium concentration on the adsorbent (mg/g), $K_L$ the Langmuir constants (L/mg) related to the free energy of adsorption, and $q_{max}$ the maximum monolayer adsorption capacity of the adsorbent (mg/g) (Gandhi et al., 2014). In other words, $q_e$ was calculated,

$$qe = \frac{Co - Ce}{m} V$$

where $C_o$ (mg/L) is initial concentration of Chromium and $C_e$ (mg/L) is concentration of Chromium at equilibrium whereas V (L) is the volume of the adsorbate and m is the mass of the adsorbent in g. In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter ($R_L$)

$$R_L = \frac{1}{1+\mathrm{KLC_0}}$$

Where $K_L$ (L/mg) is the Langmuir isotherm constant and $C_o$ (mg /L) is the initial concentration of adsorbate. There are four probabilities for the $R_L$ value: For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$ (Foo and Hameed 2010).

On the other hands, the results of adsorption were also tested using Freundlich isotherm model which was given by the following formulas.

$$q_e = K_F \mathrm{Ce}^{1/\mathrm{n}}$$

$$\mathrm{Log}\ q_e = \mathrm{Log}\ K_F + \frac{1}{n} Log\ C_e$$

$K_F$ indicates adsorption capacity (mg/g) and 1/n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The greater the values of $K_F$ better is the favorability of adsorption (Attar 2010).

**3.9. Data analysis, presentations and dissemination methods**

The results of the study were presented in the forms of tables and graphs. Moreover, the adsorption test results were analyzed using excel and IBM SPSS software. Accordingly, correlation analysis was performed using Bivariate Correlation analysis of IBM SPSS. The result of this study will be submitted to Addis Ababa Science and Technology University department of Environmental Engineering and will be also disseminated to all concerning bodies and will be published in international peer reviewed journal.

# CHAPTER FOUR

# 4. RESULT AND DISCUSSION

In this chapter the results of the study including, the adsorbent preparation and characterization, the mechanism and efficiency of chromium removal from synthetic tannery wastewater and actual tannery wastewater by prepared activated adsorbent, effects of all studied variables (pH, concentration, time, and adsorbent dose), characterization of tannery wastewater and adsorption isotherms were discussed with respect to literature in details.

## 4.1. Physicochemical characteristics of tannery wastewater

The results of some of physicochemical parameter of Gellan Tannery PLC wastewater was given by the table 3. The investigated parameters were: total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), temperature, pH, electrical conductivity (EC), biological oxygen demand of five days ($BOD_5$), and chemical oxygen demand (COD). Generally, the characterization of the wastewater indicated the high chemical Oxygen demand, and high levels of total solids. The major pollutant of the tannery wastewater is the organic matter, which was described in terms of COD and $BOD_5$. As indicated in the table 3, the tannery effluent had BOD5 of 1,462 mg/L and COD level of 1,800 mg/L.

Table 3. Some physicochemical parameter of Gellan Tannery PLC wastewater

| Parameters | Measurement result |
|---|---|
| pH | 4.32 |
| EC (mS/cm) | 29.2 |
| Temperature (°C) | 21.5 |
| DO (mg/L) | 6.58 |
| BOD5 (mg/L) | 1,462 |
| COD (mg/l) | 1,800 mg/L |

| | |
|---|---|
| TS (mg/L) | 29,000mg/L |
| TDS (mg/L) | 22,200mg/L |
| TSS (mg/L) | 6,800 mg/L |

### 4.2. Adsorbent Characteristics

#### 4.2.1. Proximate analysis

Proximate analysis is the determination, by prescribed methods, of moisture, volatile matter, fixed carbon (by difference), and ash. It is used to identify the amount of fixed carbon and non-carbons of adsorbents. Accordingly, the proximate analysis of parthenium stem activated carbon was done according to standard methods and given by percentage by weight (Table 4). As indicated in the table below; the result showed that moisture content (5.5 %), ash (19 %) and volatile substances (9.5%). The percentage of fixed carbon was calculated using the data of moisture, ash and volatile contents of the sample [100 – (5.5 + 19 + 9.5)]. So, the amount of fixed carbon found in the sample (66 %) indicated that parthenium stem can be used for the preparation of adsorbent to treat wastewater.

Table 4. Proximate analyses of activated carbon prepared from parthenium stem

| **Proximate analysis** | **Mass in %** |
|---|---|
| Moisture | 5.5 |
| Volatile matter | 9.5 |
| Ash content | 19 |
| Fixed carbon (the difference) | 66 |

#### 4.2.2. Surface area determination

Surface area of activated carbon prepared from parthenium stem ash was determined using iodine number. Iodine number is the number of milligrams of iodine adsorbed from aqueous solutions by 1 gram of activated carbon when the iodine concentration of the residual filtrate is 0.02 N. The iodine number determination of activated carbon of

parthenium stem was performed before and after the treatment of synthetic tannery wastewater. The results showed that the surface area of activated carbon was 1,213.6$m^2$/g and 256.5$m^2$/g before and after treatment respectively. Accordingly, from total surface area, only 78.86 % was occupied by adsorbate. The iodine number is affected by porosity, surface impurities and surface oxidation. Iodine number can be increased by the presence of porosity due to the larger size of iodine molecule while surface impurities such as residual oil depress the iodine number (Supriya et al. 2014).

### 4.2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis of activated carbon prepared from parthenium stem was done before and after adsorption. FTIR analysis of the activated carbon prepared from parthenium stem done before adsorption revealed three clearly observable peaks. The first broad and long peak was obtained at 3 429 $cm^{-1}$, in the range of 3 200 – 3 600 $cm^{-1}$. This broad peak represents O-H stretched form. The second peak was 1,600 which is in range of 1500 – 1600 $cm^{-1}$. This peak represents carbon-carbon double bond. The last peak of FTIR analysis of activated carbon before adsorption was 1,172 cm-1 which was in range of 1,050 – 1,300 that represents C-O single bond. On the other hand, the FTIR analysis of activated carbon done after adsorption showed only two clearly observable peaks. The first peak was at 1,583 $cm^{-1}$ which was in range of 1,500 – 1,600 $cm^{-1}$ that was C=C bond. The other peak was at 1,184 $cm^{-1}$ which was in range of 1,50 – 1,300 that represent C-O bond. The second figure 7 of FTIR analysis showed that there was interference of adsorbate with surface of adsorbent that breaks functional groups and also there was pi-pi interaction between the adsorbate and adsorbent (West 1980).

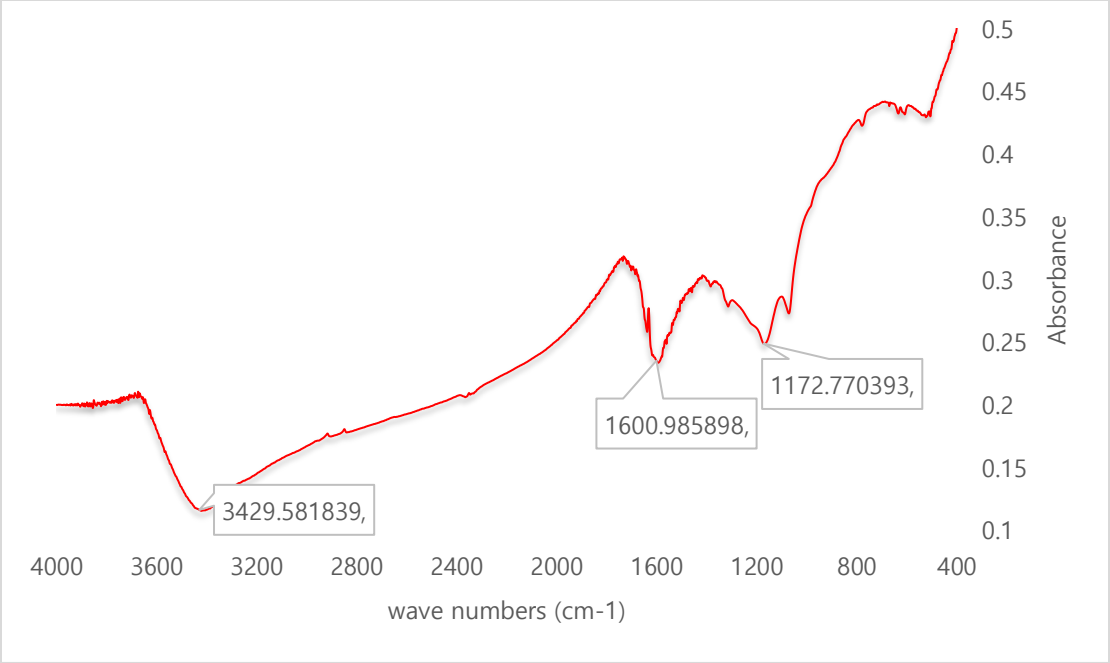


Figure 7. Infrared spectrum of parthenium stem activated carbon before adsorption.

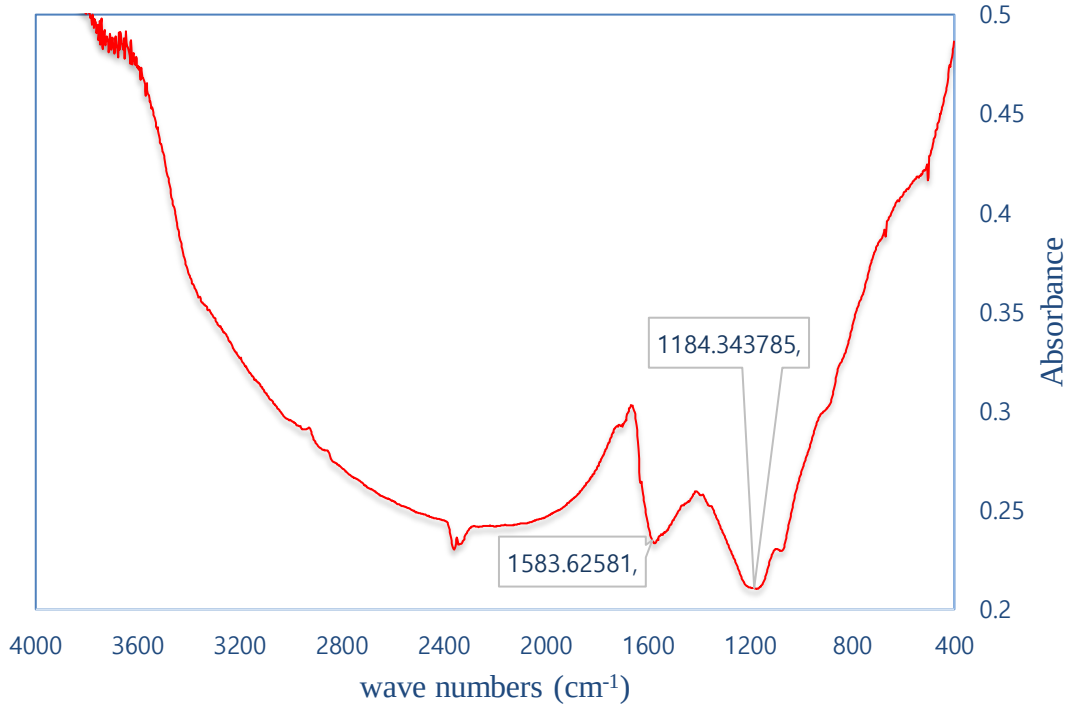


Figure 8. Infrared spectrum of parthenium stem activated carbon after adsorption

### 4.2.4. Scanning electron microscope (SEM) analysis

Scanning Electron microscope analysis was performed to see the surface morphology of the adsorbent prepared from parthenium stem. The SEM analysis was done before and after the adsorption as indicated in the Figure 8 and 9 respectively. As indicated in the image, irregular pore shape of activated carbon of parthenium stem allowed the binding of adsorbates of different sizes. This confirmed that the adsorbent was developed well and ready to interact with adsorbates of different size. Moreover, the activating chemical used during adsorbent preparation was another factor considered for effective adsorption treatment. The surface of activated carbon was magnified at different resolution; 1,000X, 16,000X, 10,000X at 5.00KV using Inspect F50 SEM analysis machine and indicated different pore size. In other way, the SEM analysis of activated carbon done after adsorption indicated that there were impurities attached to surface of adsorbent. This leads to the reduced pore size of the adsorbent after treatment.

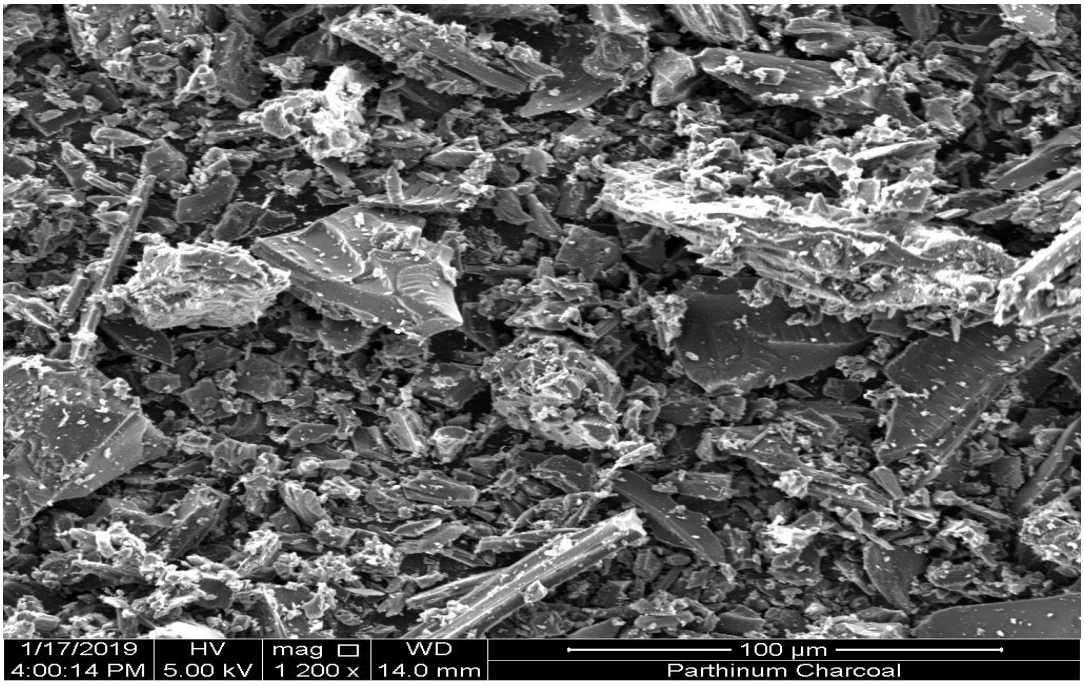


Figure 9. SEM images of activated carbon from parthenium stem before adsorption

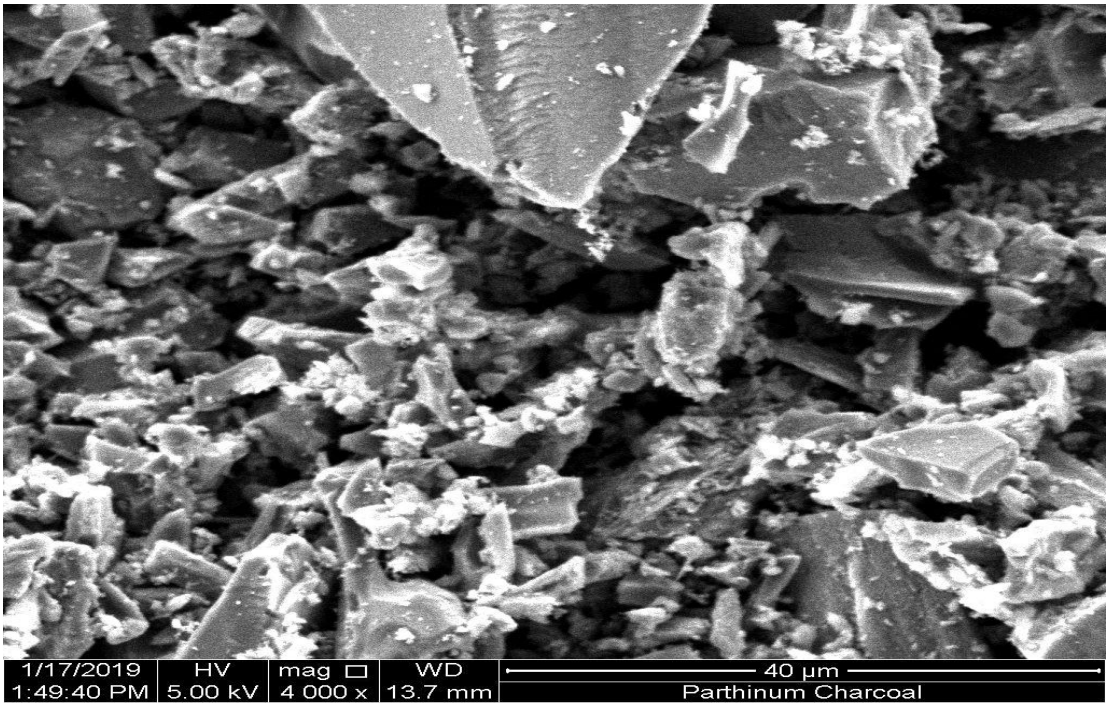


Figure 10. SEM images of activated carbon from parthenium stem after adsorption

### **4**.3**. Removal of chromium from synthetic tannery wastewater**

The adsorption treatment to remove chromium from synthetic tannery wastewater was shown using factorial matrix in Table 5 below. The maximum chromium removal (90.54%) was found at adsorbent dosage (10g/110ml), pH (2), initial Chromium concentration (100mg/L), and contact time of 90 minutes. This removal efficiency was found in the presence of interfering ions during adsorption. The synthetic tannery wastewater prepared in the laboratory was the representative of the actual tannery effluents since it was prepared from most of common impurities present in actual tannery wastewater that could interfere with attachment of adsorbate to surface of adsorbent. This was supported by the test done on sample of actual tannery wastewater taken from Modjo Tannery PLC which has initial chromium concentration of 150 mg/L. The test done on the sample showed that 89% removal efficiency at optimum adsorbent dose (10g/110ml), pH (2.00), and time (90 minutes). In other words, the test done on synthetic tannery wastewater at 150 mg/L

chromium concentration and at equilibrium values of variables showed that 94.45% removal efficiency.

Table 5. Adsorption matrix of Chromium removal from synthetic tannery wastewater

| Test | Chromium Conc. | pH | Time | Adsorbent Dose | % Chromium removal |
|---|---|---|---|---|---|
| 1 | - | - | - | - | 70.00 |
| 2 | + | - | - | - | 87.00 |
| 3 | - | + | - | - | 56.25 |
| 4 | + | + | - | - | 84.00 |
| 5 | - | - | + | - | 70.00 |
| 6 | + | - | + | - | 84.35 |
| 7 | - | + | + | - | 60.87 |
| 8 | + | + | + | - | 83.35 |
| 9 | - | - | - | + | 78.75 |
| 10 | + | - | - | + | 88.00 |
| 11 | - | + | - | + | 56.25 |
| 12 | + | + | - | + | 82.50 |
| 13 | - | - | + | + | 87.77 |
| 14 | + | - | + | + | 90.54 |
| 15 | - | + | + | + | 54.70 |
| 16 | + | + | + | + | 80.25 |
| Test done on actual tannery wastewater using equilibrium value of variables | | | | | |
| | 150mg/L | 2.00 | 90 min | 10g/110ml | 89 |

### 4.3.2. Effects of variables on Chromium removal efficiency

In order to know the effects of each independent variables on the adsorption of chromium from wastewater the batch adsorption was performed. The factorial design experiments performed used only two levels of each variables. So, to check the optimum values of the

variables in the treatment system, additional experiments were performed.

#### 4.3.2.1. Effect of initial Chromium concentration on adsorption

To know the effect of initial adsorbate concentration on adsorption, adsorbent dose (10g in 110 mL and 1g in 110ml solution), pH (2), and contact time (90 minutes) were kept constant but different initial Chromium concentrations of 40, 100, 150, 200, and 250 mg/L were taken because the target tannery wastewater has a chromium concentration between 100mg/L and 250mg/L. The temperature of the treatment system was fixed according to literature at 60°C in incubator shaker (Singh et al. 2008). It has been known that increasing the initial Chromium concentration results in an increase in the adsorption capacity because the initial Chromium concentration provides a driving force to overcome mass transfer resistances between the adsorbent and adsorption media (Özbay et al. 2013). Initially, adsorbate molecules should encounter the boundary layer effect. Then, it should diffuse from boundary layer film onto adsorbent surface and, finally, it should diffuse into the porous structure of the adsorbent (Kadirvelu et al. 2002). Therefore, at higher initial chromium concentration, the number of molecules competing for the available sites on the surface of activated carbon was high, hence, resulting in higher chromium adsorption capacities. In the case of lower concentrations, higher adsorption yields were obtained. After some ranges the adsorption percentage was found to decrease with increase chromium concentration. This may be due to the saturation of surface area and active sites of adsorbent (Arris, Bencheikh, and Miniai 2012). When 1 g adsorbent dosage was used, the adsorption uptakes of chromium ($q_e$) at equilibrium increase from 1.32 to 24.8 mg/g as the initial chromium concentration increased from 40 to 250 mg/L. But, when 10g/110mL adsorbent dosage was used, the adsorption uptakes of Chromium at equilibrium slightly

increased from 0.386 to 2.64 mg/g as the initial Chromium concentration increased from 40 to 250 mg/L. This result showed that high concentration of Chromium attained maximum percentage removal even at low adsorbent dosage. Hence, Parthenium stem activated carbon can be considered an efficient adsorbent for the removal of chromium from leather tannery industries wastewater.

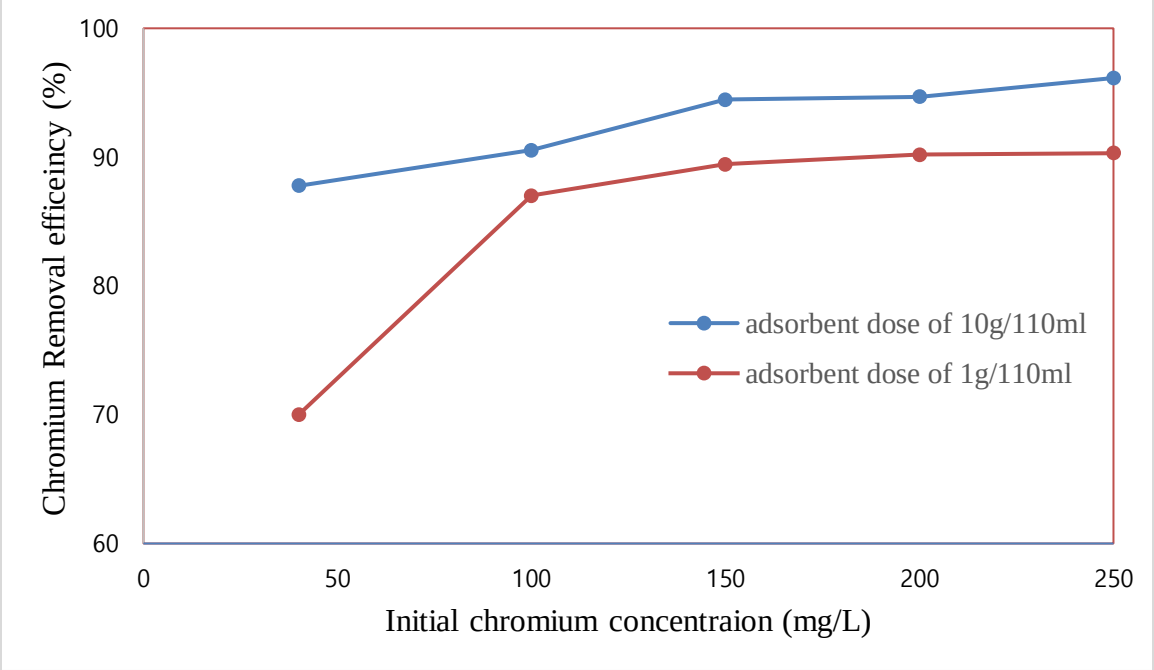


Figure 11. Effect of Initial adsorbate Concentration.

#### 4.3.2.2. The effect of pH on adsorption

The pH of the synthetic tannery wastewater plays important role in adsorption capacity, where it affects the degree of ionization of chromium as well as the surface properties of the adsorbent (Özbay et al. 2013). In this study the effect of pH was determined at initial Chromium concentration, contact time, and adsorbent dose of 100mg/L, 90 minute, and 10g/110ml, respectively. The effect of the pH on adsorption was studied at pH of 2, 3, 4, 5, and 6. the value of pH was adjusted by adding small amount of 0.1 M HCl and 0.1 M NaOH; and measured with pH multimeter. And the result showed that the adsorption

system was pH sensitive. The removal capacity of adsorbent decreased by 10.29 % as the pH of the solution increased from 2 to 6 at temperature of 60 ºC. The maximum adsorption capacity was found at pH 2. So, the pH value of 2.00 was selected as optimum for adsorption which is in agreement with previous study done on removing Chromium (VI) from aqueous solution with parthenium weed (Singh et al. 2008). An increase in solution pH releases protons from the surface and exposing more negative sites to bind more cations. In contrast, a decrease in pH protonates the surface exposing more positively charged sites on carbon to bind more anions.

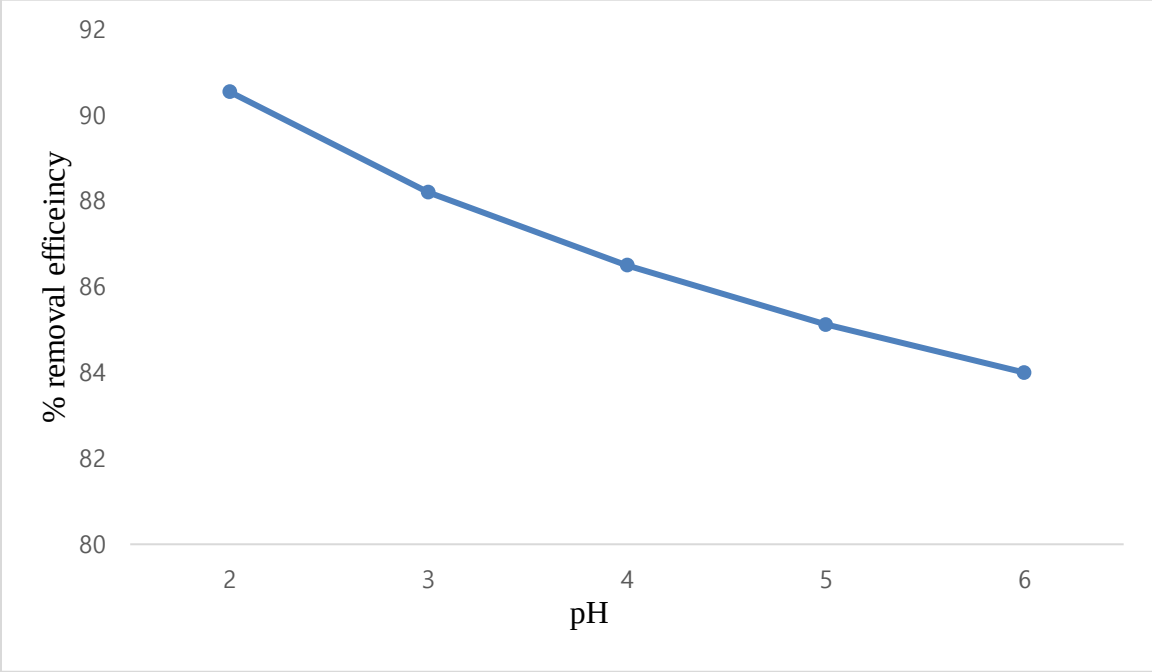


Figure 12. Effect of pH on chromium adsorption capacity of PAC

**4.3.2.3. The effect of the contact time on adsorption**

To know the effect of the duration of the time on adsorption treatment, batch adsorption experiment was carried at 60 ºC temperature, 10g/110ml adsorbent dosage, 2.00 pH, and 100mg/L initial adsorbate concentration. The result found showed that increasing contact time up to 2 hours increased removal efficiency of adsorbent. Therefore, the equilibrium

contact time of adsorption was found at 120 minutes as shown in figure 12 below. This gave enough time for adsorbate to interact with the surface of adsorbent and constant after that. Enough contact duration helps attachment of adsorbate to adsorbent surface. (Anisuzzaman et al. 2015; Bapat and Jaspal 2016; Khamis et al. 2009).

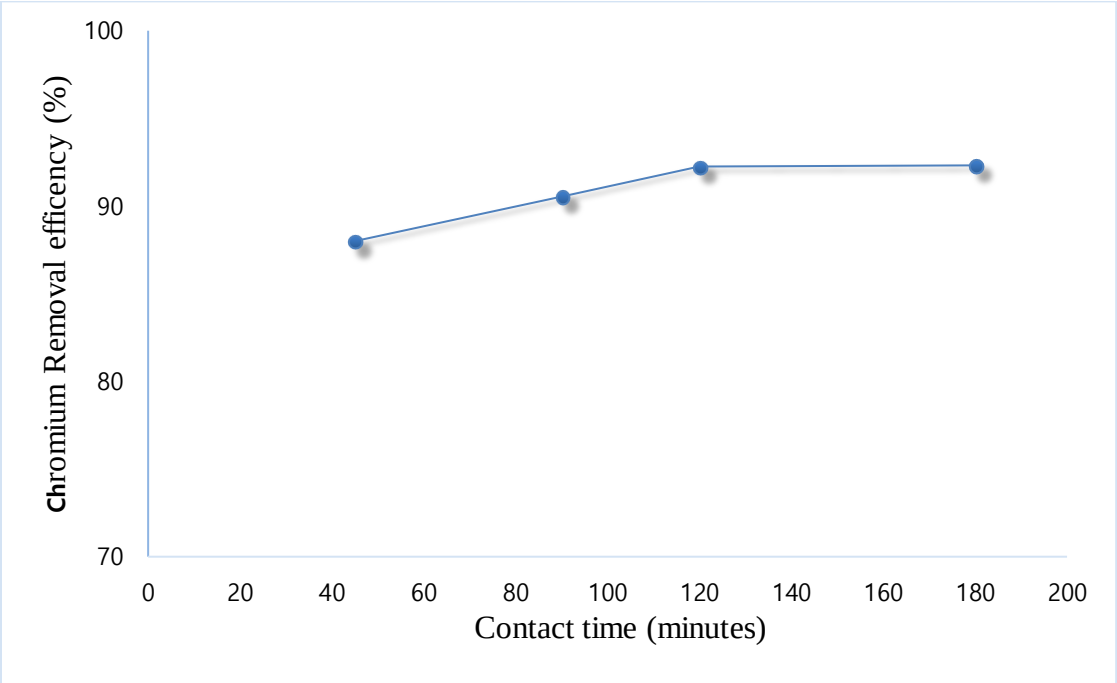


Figure 13. Effect of contact time on chromium removal efficiency of adsorbent

#### 4.3.2.4. The effect of adsorbent dosage on removal efficiency

In adsorption, the dosage of adsorbent is also very important factor to determine the potential and feasibility of specified material for adsorbent development. In this study, the removal efficiency of adsorbent was increased only by 13% as adsorbent dose increased from 1g/110ml to 20g/110ml and the total removal efficiency was found at adsorbate dosage of 20g/110L ($q_e$ = 0.55 mg/g). But at adsorbent dosage of 1g/110ml the $q_e$ value was 9.57 mg/g at optimum initial chromium concentration (100mg/L), 90 minutes contact time, pH 2. This indicated that the activated carbon prepared from parthenium stem had high

adsorption capacity even at lower adsorbent dose. When low-cost was considered, 1g/110ml solution was chosen as optimum adsorbent dosage. Increase in adsorption capacity with increasing adsorbent dosage related with increased surface area of adsorbent and availability of free sites for adsorption. But, increasing the adsorbent dosage decreased the amount of chromium uptake per gram ($q_e$). This could be explained as; First, the increase in adsorbent quantity at fixed Chromium concentration and volume will lead to unsaturation of adsorption sites through the adsorption process, and, second, the reduction in adsorbent capacity is likely to be due to particle aggregation, resulting from high adsorbent amount. Such aggregation would lead to a decrease in total surface area of the adsorbent (Nethaji, Sivasamy, and Mandal 2013).

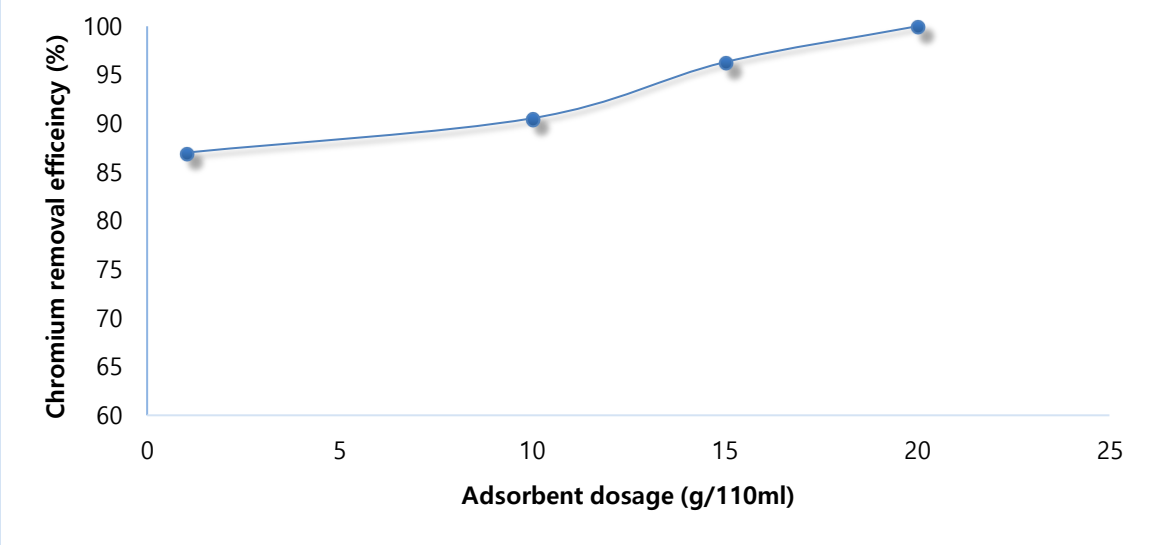


Figure 14. Effect of adsorbent dosage on chromium removal

### 4.3.3. Correlation analysis of variables

The relationships between variables during adsorption was determined using bivariate correlation analysis (Table 6). The Pearson correlation coefficient of two tailed test significance analyses were carried out and the values of the correlation coefficients (r) were

determined. The sign of the correlation coefficient indicates that the direction of the relation and the magnitude shows the strength of the relation. In this analysis, the correlation between the independent variables were zero which determined there were no relation among them. As indicated in the table 6, the relation between variables were weak because the value of correlation coefficients was less than 0.50. Strong correlation was observed only between initial Chromium concentration and Chromium removal efficiency for which the r value was 0.741 while negative correlation was found between Chromium removal efficiency and pH which was -0.501.

Table 6. Bivariate Correlation analysis of dependent and independent variables.

| | Initial Cr Concentration | pH | Time | Adsorbent dose |
|---|---|---|---|---|
| Initial Cr Concentration | 1 | .000 | .000 | .000 |
| pH | .000 | 1 | .000 | .000 |
| Time | .000 | .000 | 1 | .000 |
| Adsorbent dose | .000 | .000 | .000 | 1 |
| Cr removal efficiency | .741** | -.501* | .046 | .117 |

### 4.3.4. Adsorption isotherms

The optimum result was analyzed with both Langmuir and Freundlich models, two know models in water and wastewater treatment. First the Langmuir isotherm was used. The linearized forms of the Langmuir equation was given in the following formula.

$$\frac{Ce}{qe} + \frac{1}{qmax} Ce + \frac{1}{KLqmax}$$

where $q_e$ is the equilibrium concentration on the adsorbent (mg/g), $C_e$ the equilibrium concentration of solute in the solution (mg/L), $q_{max}$ maximum monolayer adsorption capacity of the adsorbent (mg/g), and $K_L$ Langmuir isotherm constant (L/mg) related to the

free energy of adsorption. In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter ($R_L$);

$$R_L = \frac{1}{1+KLC_0}$$

Where $K_L$ (L/mg) is the Langmuir isotherm constant and $C_o$ (mg /L) is the initial concentration of adsorbate. There are four probabilities for the $R_L$ value: For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$ (Foo and Hameed 2010). Accordingly, a plot of $C_e$ versus $C_e/q_e$ indicated in figure 14 shown that the value of $q_{max}$ calculated from slope (slope = $1/q_{max}$) was 0.57, and Langmuir constant ($K_L$) calculated from Intercept of the graph (Intercept = $1/q_{max}K_L$) was negative 0.23. From the graph the calculated value of Langmuir dimensionless constant ($R_L$) was 0.04. From the result of Langmuir constant, this model did not fit experimental data which indicates that the adsorption process was not homogenous.

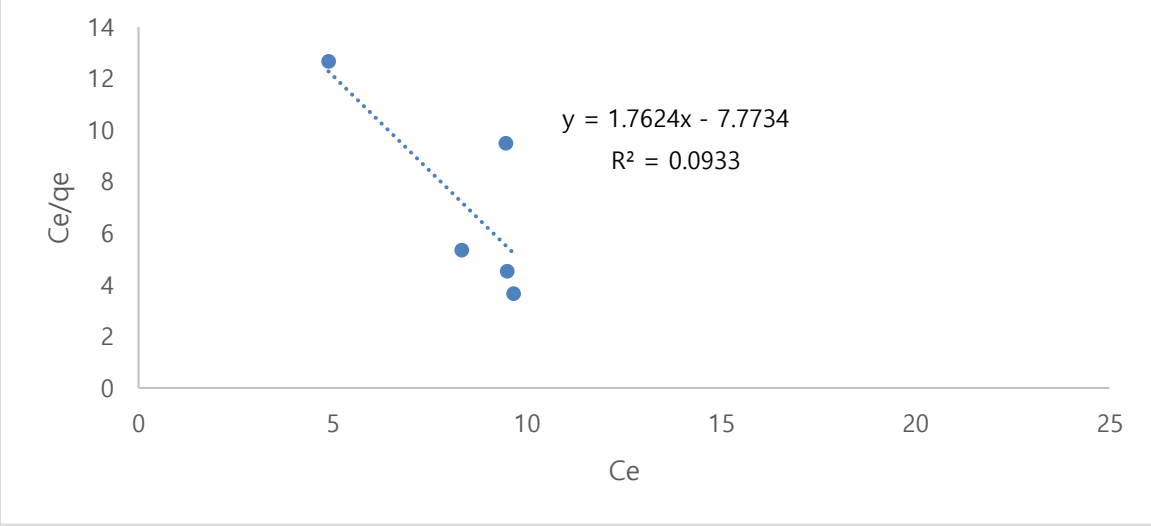


Figure 15. Langmuir adsorption isotherm at equilibrium.

The other well know isothermal model, Freundlich adsorption isotherm, was also used to

test the adsorption isotherms of Chromium removal from synthetic tannery wastewater using activated carbon prepared from parthenium stem. The Freundlich Isotherm model was given by the following formula.

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} Log\ C_e$$

where $K_F$ (L/g) Freundlich adsorption isotherm constants which indicates the adsorption capacity of adsorbent, n which is unitless related to the favorability of adsorption process and degree of nonlinearly between solution concentration and adsorption (Jemal F. Nure 2018). As indicated in Figure 15 below, graph of Freundlich adsorption isotherm model, the value of Freundlich constant ($K_F$) which was calculated from intercept of the linearized equation (log $K_F$ = intercept) was 0.01; whereas the value of n calculated from slope (1/n = slope) was 0.43 and $R^2$ value of the model was 0.78 as indicated in the Figure 15. For values of n in the range $0 < 1/n < 1$, adsorption is favorable. The greater the values of $K_F$ better is the favorability of adsorption (Attar, 2010). Accordingly, the value of 1/n (2.3) was greater than 1, so the adsorption was cooperative. The value of n calculated from the slope of the graph also indicated that the interaction between the adsorbent and adsorbate was chemisorption.

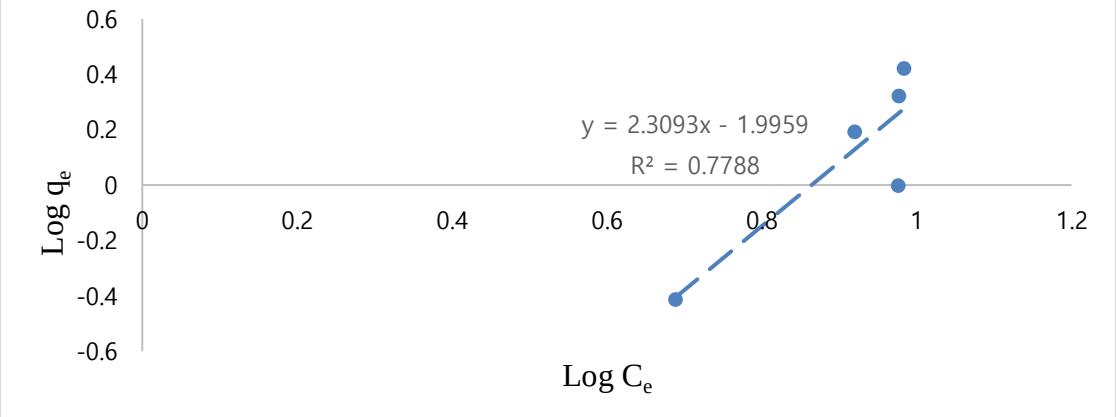


Figure 16. Freundlich adsorption isotherm of the treatment system

# CHAPTER FIVE

# 5. CONCLUSION AND RECOMMENDATION

In this chapter, what was concluded from the results of the study and the recommendation based on the result found was clearly indicated.

## 5.1 Conclusions

This factorial based study, removal of chromium from synthetic tannery wastewater using activated carbon prepared from parthenium stem, was taken place at laboratory scale at Addis Ababa Science and Technology University. The activated carbon was prepared from parthenium stem which collected from the compound of Addis Ababa Science and technology University. After preparation of adsorbent, the characterizations of the activated carbon were performed. The characterization performed were; particle surface area determination, SEM analysis, FTIR analysis, and proximate analysis. These analyses indicated that the prepared activated carbon was best fit for adsorbent preparation to treat wastewater.

The study indicated that activated carbon prepared from parthenium stem, which is abundantly available in tropical and sub-tropical area, is an effective adsorbent for removal of chromium from tannery wastewater. During optimization, four independent variables (pH, time, concentration and adsorbent dose) were studied while other parameter (agitation speed, temperature, and particle size) were kept constant based on literature. The adsorption potential is highly affected by both pH and adsorbate concentration. The optimum adsorption (90.54%) was found at pH ~2.00, time = 90 minutes, adsorbent dose = 10g/110ml, and initial chromium

concentration of 100mg/L. The pH of treatment system was practical for tannery wastewater which is basically acidic. The optimization of the treatment system was done in the presence of competing ions. After optimization, the actual tannery wastewater was taken from Gellan Tannery PLC, Modjo, Oromia, Ethiopia and the removal efficiency of activated carbon was tested using optimized levels of variables. In this case, the parthenium stem activated carbon was able to reduce chromium concentration of actual tannery wastewater from 150 mg/L to 16.5 mg/L (89%) removal efficiency. Therefore, it is likely that activated carbon prepared from parthenium stem can be used adsorbent for removal of chromium from tannery wastewater and from other industrial wastewater with the same characteristics.

The study was tested with Langmuir and Freundlich isotherms, and Freundlich Adsorption isotherm was best fitted with experimental data. The Freundlich isotherm model indicated that the adsorption was heterogenous and chemisorption.

## 5.2 Recommendations

Based on the results of this study the following recommendations were forwarded.

- As parthenium plant is widely available and demonstrate satisfactory sorption capacity, it can be used for the adsorption of Chromium from tannery wastewater.
- The efficiency of activated carbon prepared from parthenium stem in removing chromium from actual as well as synthetic tannery wastewater was good. But the efficiency in removing other competing ions (other heavy metals) needs another investigation.
- The regeneration of the adsorbent needs another study.

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# ANNEX

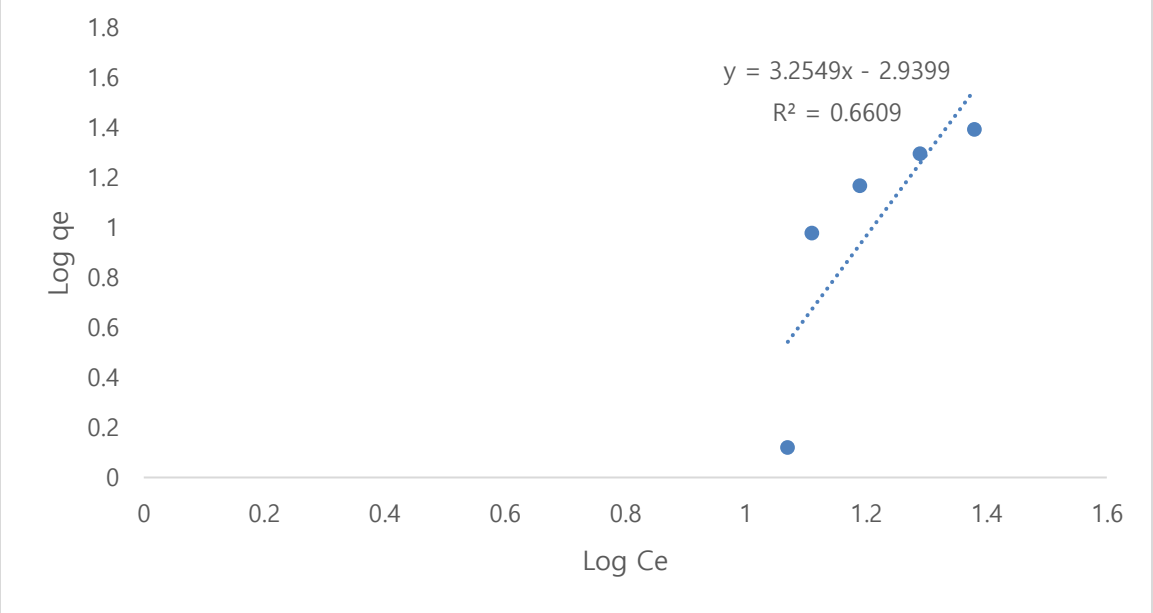
Adsorption Matrix of the treatment system

| Test No. | ABS | Initial conc. (mg/L) | Final conc ($C_e$) mg/L | $q_e$ (mg/g) |
|---|---|---|---|---|
| 1 | 1.205 | 40 | 12 | 3.08 |
| 2 | 1.319 | 100 | 13 | 9.57 |
| 3 | 2.002 | 40 | 17.5 | 2.475 |
| 4 | 1.897 | 100 | 16 | 9.24 |
| 5 | 1.236 | 40 | 12 | 3.08 |
| 6 | 1.624 | 100 | l | 9.278 |
| 7 | 1.643 | 40 | 15.65 | 2.68 |
| 8 | 1.951 | 100 | 16.65 | 9.17 |
| 9 | 1.042 | 40 | 9.5 | 0.35 |
| 10 | 1.244 | 100 | 12 | 0.97 |
| 11 | 2.057 | 40 | 17.5 | 0.25 |
| 12 | 2.008 | 100 | 17.5 | 0.91 |
| 13 | 0.541 | 40 | 4.89 | 0.39 |
| 14 | 1.160 | 100 | 9.46 | 0.996 |
| 15 | 2.181 | 40 | 18.12 | 0.24 |
| 16 | 2.318 | 100 | 19.75 | 0.88 |

Correlation analysis using SPSS

| | | Initial Cr Concentration | pH | Time | Adsorbent dose | Cr removal efficiency |
|---|---|---|---|---|---|---|
| Initial Cr Concentration | P Correlation | 1 | .000 | .000 | .000 | .741** |
| | Sig. (2-tailed) | | 1.000 | 1.000 | 1.000 | .001 |
| pH | P Correlation | .000 | 1 | .000 | .000 | -.501* |
| | Sig. (2-tailed) | 1.000 | | 1.000 | 1.000 | .048 |
| Time | P Correlation | .000 | .000 | 1 | .000 | .046 |
| | Sig. (2-tailed) | 1.000 | 1.000 | | 1.000 | .865 |
| Adsorbent dose | P Correlation | .000 | .000 | .000 | 1 | .117 |
| | Sig. (2-tailed) | 1.000 | 1.000 | 1.000 | | .666 |
| Cr removal effeciency | P Correlation | .741** | -.501* | .046 | .117 | 1 |
| | Sig. (2-tailed) | .001 | .048 | .865 | .666 | |
| **. Correlation is significant at the 0.01 level (2-tailed). | | | | | | |
| *. Correlation is significant at the 0.05 level (2-tailed). | | | | | | |

Freundlich Adsorption isotherms at 1g/110ml adsorbent and at optimum variables



**Effect of pH on chromium adsorption**

| pH | Percent removal | |
|---|---|---|
| 2 | 90.54 | At optimum initial chromium concentration (100mg/L), adsorbent dosage (10g/110ml), time (90 minutes) . |
| 3 | 88.2 | |
| 4 | 86.5 | |
| 5 | 85.12 | |
| 6 | 84 | |

**Effect of time on chromium adsorption**

| Time (minutes) | Percent removal | |
|---|---|---|
| 45 | 88 | At optimum initial chromium concentration (100mg/L), adsorbent dosage (10g/110ml), pH (2). |
| 90 | 90.54 | |
| 120 | 92.24 | |
| 180 | 92.32 | |

**Effect of adsorbent dose on adsorption**

| Adsorbent dose (g/110ml) | Percent removal | |
|---|---|---|
| 1 | 87 | At optimum initial chromium concentration (100mg/L), adsorbent dosage (10g/110ml), pH (2). |
| 10 | 90.54 | |
| 15 | 96.3 | |
| 20 | 100 | |

**Effect of initial Chromium concentration at different adsorbent dose**

| Initial chromium conc. (mg/L) | Removal efficiency in percent | |
|---|---|---|
| | adsorbent dose of 1 0g/110ml | adsorbent dose of 1g/110ml |
| 40 | 87.77 | 70 |
| 100 | 90.54 | 87 |
| 150 | 94.45 | 89.45 |
| 200 | 94.69 | 90.2 |

| 250 | | 96.14 | | | 90.3 | | | |
|---|---|---|---|---|---|---|---|---|
| Initial Chromium Conc. (mg/L) | At adsorbent dose of 10 g/110ml | | | | At adsorbent dose of 1 g/110ml | | | |
| | $C_e$ | $q_e$ | Log $C_e$ | Log $q_e$ | $C_e$ | $q_e$ | Log $C_e$ | Log $q_e$ |
| 40 | 4.89 | 0.38 | 0.69 | -0.41 | 12 | 1.32 | 1.07 | 0.12 |
| 100 | 9.46 | 0.99 | 0.96 | -0.002 | 13 | 9.57 | 1.11 | 0.98 |
| 150 | 8.32 | 1.56 | 0.92 | 0.19 | 15.82 | 14.76 | 1.19 | 1.169 |
| 200 | 9.5 | 2.08 | 0.97 | 0.32 | 19.6 | 19.84 | 1.29 | 1.297 |
| 250 | 9.65 | 2.64 | 0.98 | 0.42 | 24.25 | 24.8 | 1.38 | 1.394 |

**Iodine Number ($I_n$) was calculated by the following equation.**

$$In = \frac{X}{M} X\ A$$

Where, X = mg of iodine adsorbed by activated carbon = (12.693 $N_1$) – (279.246 $N_2$ V)

N1 = normality of iodine solution

N2 = normality of sodium thiosulphate solution

V = volume of sodium thiosulphate in ml

M = mass of activated carbon in g

A = correction factor, depending on residual normality ($N_r$) of filtrate. $N_r = N_2V/50$